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Some Leaching Characteristics of the Butte Rhodochrosite

W. L. Slosson

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Slosson, W.L.

SOME LEACHING CHARACTERISTICS OF THE BUTTE RHODOCHROSITE

by

W. L. Slosson

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

Montana School of Mines
Butte, Montana.

May 1, 1942.

MONTANA SCHOOL OF MINES LIBRARY.

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INTRODUCTION

With the increasing importance of manganese in the metallurgical fields of today and tomorrow, extensive work along the lines of its successful exploitation has been accomplished by many investigators. Since the current world situation has shut off most of our supply of high-grade manganese ores from foreign sources, the low-grade domestic deposits have entered the fields of investigation very rapidly.

The Engineering and Mining Journal Current Metal Statistics Report for 1941 states: [3 **] .....

"Shipments of manganese ore (35 percent or more manganese, natural) from domestic mines are estimated at 76,000 long tons in 1941, compared to 40,123 long tons in 1940.

"Manganese ore was reported shipped from Alabama, Arizona, Arkansas, California, Colorado, Georgia, Idaho, Montana, Nevada, Oklahoma, Oregon, Tennessee, Utah, Virginia, Washington, and West Virginia. However, Arkansas, Montana, and Tennessee accounted for about 77 percent of the total in 1941. There were no shipments from Puerto Rico in 1940 and 1941.

"Shipments of ferruginous manganese ore (10 to 35 percent manganese, natural) from domestic mines are

** All references listed in Bibliography.

estimated at 459,000 long tons in 1941, compared with 320,000 long tons in 1940. Ferruginous manganese ore was shipped from Alabama, Arizona, Arkansas, Georgia, Idaho, Massachusetts, Minnesota, Montana, Nevada, New Mexico, North Carolina, Oklahoma, Tennessee, Virginia, Washington, and West Virginia. New Mexico and Minnesota, however, contributed about 93 percent of the total in 1941.

"Shipments of manganiferous iron ores (5 to 10 percent manganese, natural) from domestic mines are estimated at 820,000 long tons in 1941, compared with 816,541 long tons in 1940. Manganiferous iron ore was shipped from Minnesota and Nevada in 1941.

"General imports of manganese ore containing 35 percent or more manganese during the nine month period ending Sept. 30, 1941, comprised 838,239 long tons of metallurgical ore, containing 393,741 tons of manganese; and 14,951 tons of battery-grade ore, containing 7,869 tons of manganese.

"Current prices on manganese ores are as follows:

Manganese ore (foreign) c.i.f., U.S. ports, long ton unit:

52 @ 55 percent	------	(b) 70¢
50 @ 52 percent	------	(b) 68¢
46 @ 48 percent	------	(b) 66½¢

Quotations cover wholesale lots, prompt shipment, f.o.b., New York, unless otherwise stated - as of Feb. 2, 1942.

"(b) --- not quoted." .....

Mr. B. W. Corrado, in his summaries of last year, stated:[2] .....

"The reserves of manganese ore in the U.S., of other than the so-called 'high-grades', have been estimated to be so great as to outlast the nation's reserves of iron ore. This, however, is on the basis of using manganese ores with quite low manganese content, for example with 25 percent of manganese instead of 50 percent, and including ore of even lower grade such as the South Dakota spathic manganese ore with about 16 percent each of manganese and iron." .....

According to John B. Huttl,[8] the annual requirement of manganese ore or concentrate of ferromanganese grade in the United States is around 1,250,000 tons. In his report, he outlines the new manganese plant at Anaconda, Montana, which is now processing the low-grade manganese ores of the Emma Mine in Butte, Mont. The Anaconda plant, by means of flotation concentration,

followed by kiln treatment and nodulizing, has succeeded in producing a ferro-grade manganese oxide, containing approximately 58 percent manganese, and highly desirable for the production of ferromanganese. The low-grade deposits of the Emma Mine are at the present carrying approximately a 21 percent manganese content.

The recent development of the electrolytic manganese processes has for the first time provided metallurgists with an adequate supply of high-purity manganese. The possibility of making commercial alloys relatively free from aluminum, carbon, copper, iron, and silicon has been made a reality. By use of high purity manganese, several alloy systems have been examined and their physical properties determined. In general, however, sufficient investigations have not been completed to realize the full significance of the manganese alloys. [12]

The Department of the Interior, Information Service Bulletins, Feb. 17, 1942, [15] states that recommendations for manganese development sufficient to produce approximately 2,683,000 long tons of manganese metal, enough for 429,000,000 tons of steel, and providing for the establishment of eight large milling plants,

three hydro-metallurgical processing plants, and one matte smelting plant; all of which would save 1,112,680 tons of shipping per year from Brazil and Cuba to the United States. Deposits in 13 districts of 8 states would furnish the necessary tonnage.

PREVIOUS INVESTIGATIONS

Since much work has been accomplished on electrolytic manganese during the last few years, the various and many problems connected with the advantageous treatment of the different manganese ores have arisen throughout the investigations, and many of these problems are still under study and surveillance.

The largest share of the investigations have been under the supervision of the U.S. Bureau of Mines, who have been following up their investigations from the last World War until the present.

During the last war period, from 1916-1918, the U.S, Bureau of Mines conducted a series of tests on manganese uses, preparation, mining costs, and the production of ferro-manganese alloys.[1] They found that the various higher manganese oxides, especially pyrolusite, psilomelane, and wad were found to be readily soluble as sulphates in hot sulphurous acid, formed by introducing hot air or furnace gas containing 2 to 6 percent sulphur dioxide (by volume) countercurrent to a pulp flow having a consistency of two of water to one of ore crushed to twenty mesh. Manganite and braunite were found to be not commercially soluble, and silicates of manganese were found to be insoluble in sulphurous acid at atmospheric pressure and only

slightly soluble under pressure. They found that carbonates of manganese may, from an operating standpoint, be considered insoluble. The sulphur dioxide slowly attacks and decomposes the carbonate, but some of the dissolved manganese at once re-precipitates as a sulphite; this precipitate coats the remaining undissolved carbonate and effectually prevents further dissolution.

Most previous work has been done on roasted oxide ores, but unlike manganese dioxide, manganese carbonate will react with sulphuric acid to form manganous sulphate. Therefore, no roasting would be required before leaching, provided that the carbonate ore can be leached at an economical rate with dilute sulphuric acid. On the other hand, manganese carbonate, like manganese dioxide, can be roasted in a reducing atmosphere to form manganese oxide.

U.S. Bureau of Mines tests on the Butte rhodochrosite ores stated:[13] .....

"63.5 percent of the manganese could be dissolved in the dilute sulphuric acid-ammonium sulphate solution after eighteen hours agitation at room temperature, but 98.0 percent of the manganese content could be dissolved in two hours agitation at 75°C.

"It is concluded that rhodochrosite ore can be leached satisfactorily without roasting, provided that the solution is heated above room temperature. No detailed studies have been made." .....

Work designated by the Technologic Committee on Manganese of the National Research Council, National Academy of Sciences, has been conducted to determine the practicability of recovering a ferro-grade product from the manganese carbonate nodules of Chamberlain, South Dakota, by the Reyerson modification of the sulphur dioxide leaching process.[16] This modification depends upon the use of a large excess of air to oxidize sulphur dioxide to sulphur trioxide in solution. Dilute sulphuric acid readily dissolves the manganese carbonate in the nodules. All of the calcium carbonate and much of the magnesium carbonate are also dissolved.

From the discussion by the U.S. Bureau of Mines, relating to the above investigations, we find:[5] ....

"Attempts to produce dilute acid in the washings from the filtration step were not successful. Drum leaching tests employing a slurry of nodules consisting of one part of -65 mesh nodules to 2.50 parts of

water also were unsatisfactory. The most promising results were obtained with a spray leacher, which gave extractions of 80-85 percent of the manganese in a two-hour treatment period.

"Work also has been done on the evaporation of crude manganous sulphate solutions and on the calcination of manganous sulphate to produce a ferro-grade product, recovering the sulphur for re-use in the leaching step." .....

The U.S. Bureau of Mines, in its Report of Investigations 3406, July 1938,[13] presented the first information on the successful electrolytic plating of manganese. The process, as outlined by the Bureau of Mines, was adaptable to commercial operation, with the result that the Electro-Manganese Corporation constructed a small plant at Knoxville, Tennessee, to produce electrolytic manganese. This plant is at the present producing 2 tons electrolytic manganese per 24 hours, having gone through the pilot-plant stage successfully and is now in regular production.

According to R. S. Dean,[4] as far as its flow sheet is concerned, the electrolytic manganese process is quite simple. The preferred form of manga-

nese for introduction into the electrolyte is manganous oxide, which may be satisfactorily prepared from the dioxide ores by a reducing roast at a temperature of 500° to 550°C. At this temperature, the iron in the ore is reduced to its most insoluble form, Fe_3O_4. Moreover, the manganous oxide so produced is less subject to reoxidation in air than if reduced at higher temperatures. The manganous oxide thus formed is readily soluble in dilute sulphuric acid, and the pH of the resulting solution may be brought as high as 6.0 without using an excessive time for leaching.

Mr. Dean further states in his report that manganese carbonate is also suitable for introducing manganese into the electrolyte. The carbonate, particularly in its naturally occurring form, is less soluble than manganous oxide, consequently it is difficult to bring the final leach to a pH sufficiently high enough to precipitate the iron. When manganese carbonate is used to feed an electrolytic circuit, it is therefore necessary to complete the neutralization with manganous oxide or lime, thus involving a loss of sulphuric acid.

According to summaries of recent investigations by the U.S. Bureau of Mines,[5] the desirable features of being able to produce electrolytic manganese are as follows: .....

"(1) The metal can be produced from low-grade domestic ores, which are of no value as ferromanganese ores.

"(2) The metal is very pure, assaying approximately 99.90 percent manganese. Previous to this, thermite manganese, assaying 95-96 percent manganese, was the purest manganese available. This feature is very important, as it has been proved in many industries that the purer the metals, the better the products obtained therefrom.

"(3) The selling price of thermite manganese has been roughly 36 cents a pound, whereas, it is estimated that in large-scale operation the cost of electrolytic manganese will be less than 10 cents per pound. Therefore, industry in the United States will have at its disposal a purer metal at a reduction in cost. This feature alone will promote the use of many new alloys.

"(4) Most important, electrolytic manganese can be used as a substitute for ferromanganese in

steel and thus assist in making the United States independent of the foreign sources of high-grade manganese ores." .....

A new research laboratory was put into operation[5] by the U.S. Bureau of Mines, at Boulder City, Utah, in April, 1941, and since then approximately 100 individual electrolytic cell runs have been completed.

The research work has been divided into three divisions, that is, reduction roasting, leaching and purification, and electrolysis.

The ore used in the above work was from the Three Kids mine near Las Vegas, Nevada. Research work on other ores will be undertaken in the near future.

Investigators at Boulder City state:[5] .....

"The reducing-roast experiments, using various reducing agents, point toward very satisfactory reduction with either fuel oil or gases. Data on reduction temperatures, size of ore, fuel consumption, etc., are being obtained.

"Leaching of reduced Three Kids ore has presented no difficulties. Excellent extractions can

be made by using a two-stage leach, whereby the first leach is made for pH control, and the second leach for manganese extraction. Pertinent operating data essential for the pilot plant operations are being obtained.

"Purification of solutions before electrolysis has been satisfactory. New purification methods and controls for plant operations are being worked out.

"The electrolysis of the solutions has received considerable attention. Special thought has been given to the design of the electrolytic cells in order to facilitate plant control.

"Particular attention has also been given to the various concentrations of ammonium sulphate and manganese, current densities, and pH of plating solutions.

"At present, satisfactory and promising results have been obtained from using higher current densities with simultaneous plating from solutions at a pH of 6.0. It is the intention to continue work along the conditions as outlined in previous Bureau of Mines publications[13,6] and, at the same time, investigate the possibilities of other plating conditions." .....

Upon the results established by the Research Laboratory, a hydro-metallurgical and electrolytic pilot plant was built at Boulder City, Nevada, and is investigating the practicibility of these results.

PROBLEM

My problem is chiefly concerned with the leaching characteristics of the rhodochrosite ores of the Emma Mine in the Butte, Montana district. Since this is a carbonate ore, chiefly manganese carbonate, the sulphur dioxide method of leaching used by the U.S. Bureau of Mines[16,1] would be unfavorable for my investigations. Due to the fact that this type of ore is readily amenable to leaching with dilute sulphuric acid solutions, conforming to acid concentrations and conditions of spent electrolyte, sulphuric acid as the leaching agent is to be considered in all of my work.

In the studies of most of the references listed in this report (see page 56-57) I found no detailed data or information concerning results of sulphuric acid leaching of this type of ore. Lloyd Thompson, M.S., 1941, Montana School of Mines, in his work on "Electrowinning of Manganese from Rhodochrosite",[14] gave some very interesting data on his leaching results using dilute sulphuric acid solutions as the leaching agent. My work is intended to expand this data and further investigate the leaching properties and characteristics of the ore under study.

There are many problems to be surmounted in the leaching of any ore, and manganese is no exception, but, rather, an excellent example of the difficulties encountered. My purpose is to study a few of these problems, with respect to varying acid concentrations, varying mesh size of ore, varying time limits, and varying temperatures favorable to practical leaching of the material.

During the tests, I did not endeavor to fully take into consideration every variable encountered in turn, but rather the investigations were run in such a way as to incorporate all varying conditions into the series in such a manner as to give a good comparison background to the results.

Since previous tests by the U.S. Bureau of Mines yielded very low recoveries on 18-hour leaching rests at room temperature (20°C.),[13] and Mr. Thompson verified these results,[14] very little work was done on my part concerning leaching at room temperature except to run five preliminary tests confirming previous investigations at this temperature.* I accomplished the greater part of my tests at elevated temperatures varying from 60°-90°C.

In my test results I was interested mainly in

* See Table 2.

the presence of manganese, iron and free acid in the recovered solution. The recovery of manganese was considered mainly to govern the efficiency of the leaching procedure and to tie in with the free acid content in the leach liquor, thereby giving the acid consumption regarding the efficiencies attained. I took the recovery of the iron into consideration because of its value as an agent in the subsequent purification steps on the leach solution. In collaboration with pH control, that is in a range of approximately 5.3 or slightly over, the iron present after oxidation to the ferric form, will come down as the ferric hydroxide and bring the arsenic present in the leach solution down with it in accordance with the following equation:

$$4Fe(OH)_3 + H_3AsO_3 \longrightarrow Fe_4O_5(OH)_5As\downarrow + 5H_2O$$

This important step is accomplished in the iron-arsenic precipitation tank where NH_3 or CaO is added to bring the pH values up to the required point for iron-arsenic precipitation according to the above figure.

Low acid concentrations were kept in mind in order to maintain better control of values and to assume conditions of leaching with spent electrolyte or solutions of the same strengthened by addition of further acid. The tests made by the U.S. Bureau of Mines at Reno, Nevada,[13] indicated that leaching with spent electrolyte was desirable. Their laboratory tests show that at least 99.0 percent of the manganese content in the ore can be leached readily with a two-stage leaching procedure using the spent electrolyte, containing 30 grams per liter of sulphuric acid, on the first stage, and a stronger concentration of acid on the second stage. However, all of my tests were of single stage leaching to determine its possibilities, and the acid concentrations were adjusted to facilitate complete removal of manganese content of the ore under ideal conditions.

The problem in mind, therefore, is summarized as follows:

(1) A study of the effects of varying time limits, temperature ranges, size of ore, and acid concentrations upon the efficient and favorable

leaching of the ore under investigation.

(2) A study of pH control and minimum acid requirements to yield the most economical leaching results.

(3) All above problems to be directly concerned with single stage leaching procedures.

LEACHING EXPERIMENTAL WORK

In all leaching investigations, ore from the Emma Mine was used. Since this ore was mined and hoisted in 1936, the 38.4 percent manganese content is considerably higher than that present in the same ore today. The ore being hoisted from the Emma Mine at the present contains approximately 20.0-22.0 percent manganese.

After being crushed in a laboratory size gyratory crusher set for a one-fourth inch discharge, the ore was coned and quartered into several samples. A portion of each sample was then crushed by means of a coffee-mill type crusher, followed by a bucking table, until the sample would pass through a designated screen size. The screen sizes were respectively, 6, 28, 65, and 100 mesh, based upon the Tyler screen scale. Screen analyses were run on each sized sample. The results of the screen analyses are tabulated in Table 1 on the next page. Each sized sample was then set aside for subsequent leaching tests.

An analysis of the ore was made, and the results are as follows:

	Percent		Percent
Mn	38.40	Cu	0.00
Fe	1.65	Insol	8.50
Zn	5.30		

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Mesh	Wt. gm.	Wt. percent	Cum. percent	Wt. gm.	Wt. percent	Cum. percent	Wt. gm.	Wt. percent	Cum. percent	Wt. gm.	Wt. percent	Cum. percent
	All thru 6 mesh			All thru 28 mesh			All thru 65 mesh			All thru 100 mesh		
+6	0.0	0.0	0.0									
+8	77.6	15.3	15.3									
+10	93.9	18.6	33.9									
+14	65.3	12.9	46.8									
+20	47.8	9.5	57.3									
+28	47.0	9.3	66.6	0.0	0.0	0.0						
+35	27.3	5.4	72.0	67.5	18.6	18.6						
+48	27.0	5.3	77.3	59.2	16.4	35.0						
+65	22.6	4.5	81.8	46.3	12.8	47.8	0.0	0.0	0.0			
+100	20.7	4.1	85.9	40.5	11.2	59.0	68.7	27.3	27.3	0.0	0.0	0.0
+150	16.1	3.2	89.1	32.0	8.8	67.8	52.2	20.7	48.0	141.2	28.5	28.5
+200	13.1	2.6	91.7	28.5	7.9	75.7	28.5	11.3	59.3	106.8	21.6	50.1
-200	47.0	9.3	100.0	88.0	24.3	100.0	102.0	40.7	100.0	245.6	49.9	100.0
Total	505.4	100.0		362.0	100.0		251.4	100.0		493.6	100.0	

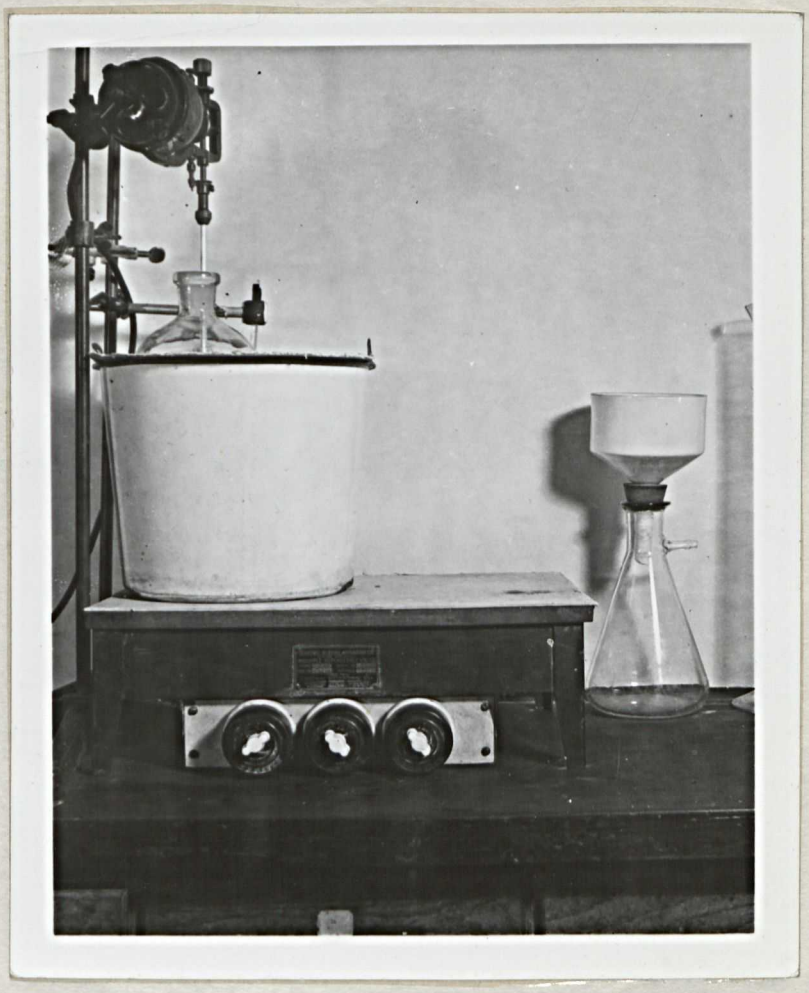
SCREEN ANALYSES OF ORE USED IN TEST WORK

(Note) A coffee-mill type crusher was used to crush the ore all through 6 mesh; to get the remaining samples through their designated screen size, a bucking table and hammer was employed, which probably accounts for the larger percentage of finer material in the smaller mesh sizes used.

Table 1.

From the U.S. Bureau of Mines analysis of the same type of ore from the Butte district,[13] the presence of arsenic, nickel, cobalt, calcium carbonate, and magnesium carbonate were also noted in minor amounts. However, these constitutents did not immediately enter into my consideration during the actual leaching tests, and for this reason they were not considered as strongly affecting the leaching properties of the ore except as leach-resistant materials and acid consumers. Their small amounts in the ore did not account for an exact analysis in my studies. The effects they did show upon the leaching properties of the ore will be discussed later. The above impurities are very important in forming a purification of the leached solution for subsequent electrolysis, and this fact should be kept in mind at all times during any leaching procedure.

A leaching unit was constructed with laboratory equipment. (See Plate I) A standard 110-volt, 3-unit hot plate was used for the heating purposes. To maintain a constant temperature, two 2-gallon buckets were filled with water and



Leaching Unit

Plate 1.

brought to the desired temperature. One bucket of water was used just as a stabilizer for a constant temperature,* and the other was used to heat the leaching solution. The solution was then placed in a Winchester bottle and immersed in the designated water bath. This bucket was covered with an asbestos cover provided with openings for the top of the Winchester bottle and a thermometer. A small 110-volt, laboratory size stirring motor equipped with a glass stirring rod terminated with a short length of rubber tubing served as the agitating unit. The presence of the two-inch length of rubber tubing on the immersed end of the glass rod greatly improved the agitating action of the rotating stirring mechanism. An auxiliary air agitation unit, consisting of a length of tubing attached to a glass rod and connected to the compressed air line, was kept available in case of motor or power failure. This apparatus, although crude and simple, afforded very satisfactory performance and fairly uniform operating conditions.

All leaches were made in one liter of solution brought up to the desired acid, ore, and ammonium sulphate concentration.

* Not shown in Plate I.

The extent of ore crushing and grinding is largely dependent upon the texture of the ore to be treated. Highly efficient leaching may be expected from a porous ore ground to -10 mesh or coarser, but a dense ore requires finer grinding. Since I discovered better leaching efficiencies upon using a finer grind, that is, -65 or -100 mesh, I found the Butte rhodochrosite to be of the denser type of ore.

Leaching reagent is regenerated in the electrolytic process. The loss of acid in leaching depends largely on acid-soluble alkaline metals in the ore. Measurements made by the U.S. Bureau of Mines [13] showed a loss of acid due to impurities on one type of ore to be approximately twenty pounds of sulphuric acid per one hundred pounds of electrolytic manganese. In the electrolytic cell, anodic manganese dioxide reacts readily with sulphur dioxide-water solution to form manganese sulphate. The loss of sulphate ion as sulphuric acid and as ammonium sulphate can be replaced in this manner and at the same time the proportion of manganese dioxide to manganese metal formed as a process product will be reduced proportionately.

According to U.S. Bureau of Mines statements, a high concentration of ammonium sulphate is used because: [13].....

"(1) In the subsequent electrolytic cell, resolution of the deposited metal is encountered less frequently, provided that the ammonium sulphate concentration is 100 grams per liter or greater in the almost pure solution.

"(2) The flow of current between the anode and cathode is through a conductive acidic anolyte, through a cloth diaphragm, and through a basic catholyte. All of the metallic manganese deposition takes place with one pass through one catholyte chamber of one cell. Consequently, high metal recovery necessitates low manganese sulphate concentration in the catholyte chamber. Manganese sulphate solution is a relatively poor conductor of electricity, particularly at low concentrations. The high ammonium sulphate concentration serves to reduce ohmic resistance in the catholyte solution and provides lower cell voltage and, consequently, lower power consumption." .....

From the ternary diagrams [11] reproduced in Plates II-A and II-B, it is shown that the solu-

bility of manganous sulphate in a solution of ammonium sulphate is definitely limited if excessive crystallization is to be prevented. U.S. Bureau of Mines work[13] has shown that $(NH_4)_2SO_4$ present in a greater concentration than 125 grams per liter has no beneficial effect upon the bath and that concentrations from 150-200 grams per liter provide a good working range.

Although I performed no electrolysis experiments in my leaching investigations, I incorporated ammonium sulphate into the leaching tests so as to get results conforming to those accomplished in an electrolytic plant leaching operation. Throughout my investigations, I use 150 grams of ammonium sulphate per liter in all tests where the presence of this reagent was designated.

Since the U.S. Bureau of Mines limited their manganese sulphate concentration in the catholyte feed to less than seventy grams per liter (equivalent to twenty-five grams of manganese per liter) because it was believed desirable to limit the sulphuric acid concentration of the anolyte and thereby protect the cloth diaphragm, all tests were made with the idea in mind of keeping the manganese

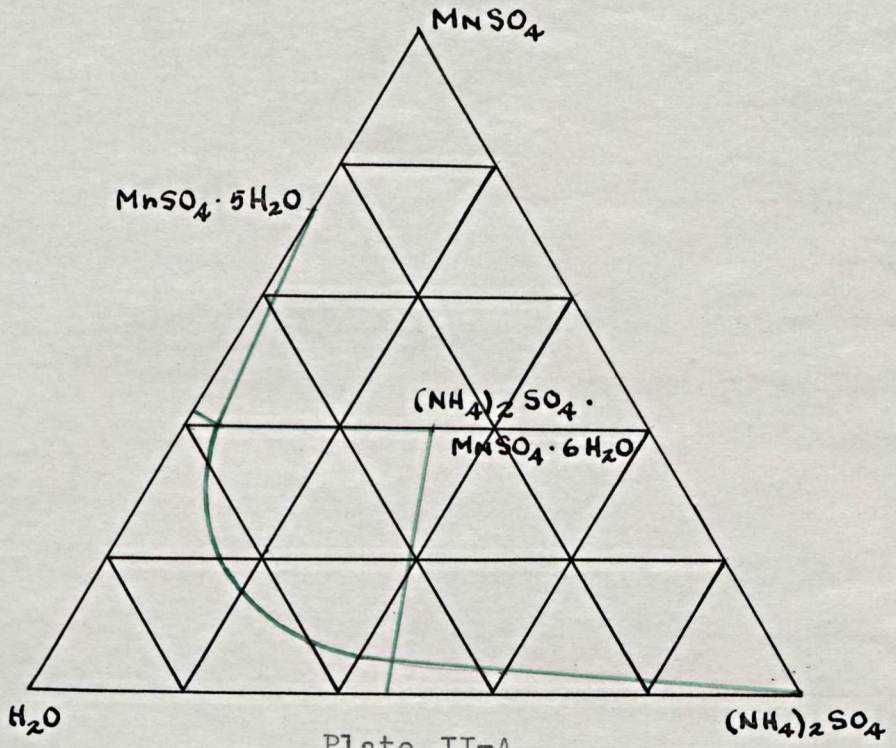


Plate II-A

Ternary System: H_2O - $(NH_4)_2SO_4$ - $MnSO_4$ (at 25°C)

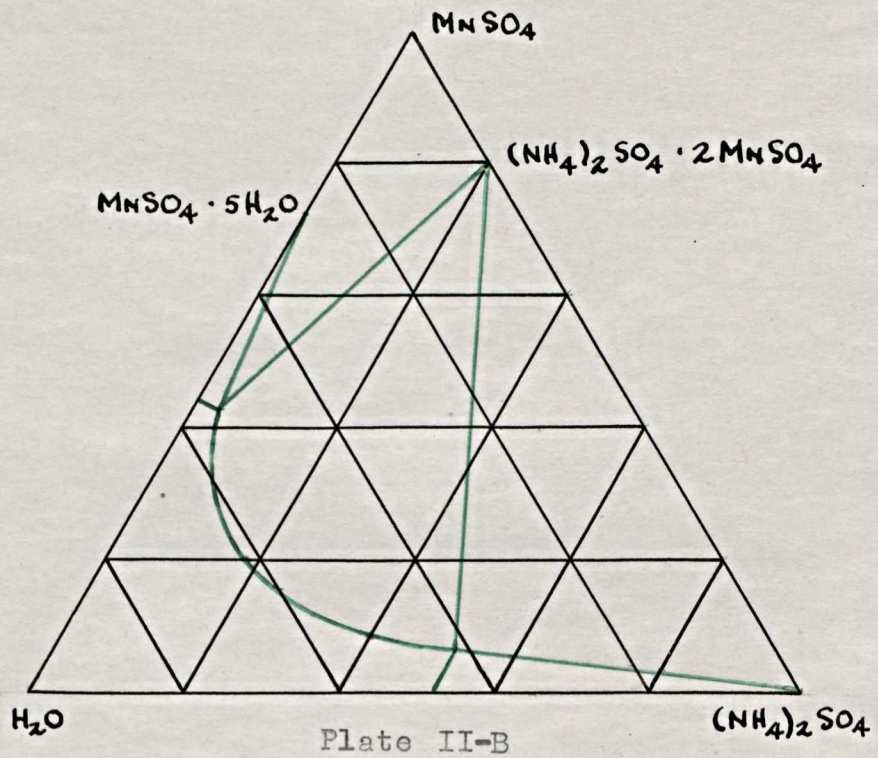


Plate II-B

Ternary System: H_2O - $(NH_4)_2SO_4$ - $MnSO_4$ (at 50°C)

sulphate around the above figure. Increase in manganese sulphate concentration would require a decrease in ammonium sulphate concentration if the solubility limits are to be avoided to the same degree. The changes would affect the resistances of both the catholyte and anolyte. The relationship with the ultimate effect on cell operation is being studied by the U.S. Bureau of Mines.[13]

Two series of the leaching procedure were run with a large excess of sulphuric acid over the theoretical requirement to leach to the neutral point with 100 percent recoveries. The temperature was varied on each series so as to gain some knowledge upon the behavior of the leach under different temperature conditions. All other conditions were held constant in both series with the exception of the time of leaching and mesh size of the ore. (See Tables 3 and 4)

Another leaching test was run with the purpose in mind of finding the most economical conditions for leaching to beneficial manganese recoveries in the leach liquor. If the ore under investigation were 100 percent $MnCO_3$, calculations show that 55.3

grams of sulphuric acid per liter of leach solution would be required to obtain the neutral point with 100 percent recovery on 65 grams of the ore, this being the weight of 38.4 percent ore to give 25 grams of manganese per liter. Since $MnCO_3$ contains 47.8 percent manganese, and assuming that all the 38.4 percent manganese content of the ore is present as $MnCO_3$, further calculations showed that 44.0 grams of sulphuric acid per liter are required to leach 25 grams of manganese into solution as manganous sulphate, assuming 100 percent recoveries. These calculations showed that the ore was composed of about 80 percent $MnCO_3$. A manganese concentration in the leached solution of 25 grams per liter, is as stated before, equivalent to 70 grams of manganese sulphate per liter. With these two acid concentrations in mind, I ran the series of tests using the best leaching conditions previously determined and derived form Tables 3 and 4, mentioned in the preceeding paragraph. By varying the acid concentration on each set of tests, I endeavored to reach an optimum acid requirement for successful leaching to high recoveries. A control of pH on the resulting solutions was undertaken

in order to observe the results of the narrowing field of acid concentrations upon pH values corresponding to beneficial recoveries. (See Table 5)

In all testing procedure, analyses of the ore and pregnant solution were accomplished by the regular methods. The manganese and iron recoveries were calculated from results of the analyses of manganese and iron content of the pregnant solutions.

A shortened arsenious acid method for the manganese, and a shortened potassium dichromate method for the iron were employed in their tests. A standardized NaOH solution was prepared for the free acid determinations, and methyl orange was used for the indicator. Methyl orange was chosen because its transition point is in the pH range of 4.00-5.00, which is very close to the precipitation point of $Fe(OH)_3$, that is, 5.30, and which point was considered the neutral stage in my work. All pH determinations were made by means of a Beckman Laboratory pH-Meter. This apparatus employs the use of a glass-electrode, and is very sensitive to pH changes of ± 0.01.

All leached solutions were filtered in a pressure filter before analysis and the residue discarded.

DISCUSSION OF RESULTS

Effect of Temperature and Leaching Time

From a comparison of Tables 2, 3, and 4, it is apparent that elevated temperatures are desirable in obtaining beneficial recoveries of manganese, with acid concentrations well above the theoretical requirements previously stated. (See p. 29-30) The results of these tables are brought out more vividly by Plates III, IV, and V, whereupon the plotted curves show the effect of leaching temperature and mesh size of ore used in regards to leaching time.

The data from Table 2 and corresponding data from Tables 3 and 4 concerning the -65 mesh ore, was compiled into Plate III to show the effect of temperature and leaching time upon the recoveries of manganese, all other influences remaining constant. It is seen from this diagram that higher temperatures are definitely favored in obtaining beneficial recoveries with 2-hour leaching periods. There appears to be no doubt whatsoever as to the leaching possibilities of the ore at elevated temperatures, and a very definite increase in recoveries is shown at these temperatures. Leaching at room temperature may bring good recoveries, but the time element would destroy any value of

the attainment of these recoveries, as leaching for 12 hours with -65 mesh ore at room temperatures (20°- 25°C) yielded only 50.0 percent manganese recoveries.

Effect of Ore Size Used in Leaching

From observation of Plates IV and V, it is seen that a finer grind, preferably all through 65 or 100 mesh, gives the best recoveries in both temperature ranges of leaching. Evidently, the fact that the ore is fairly dense and friable accounts for this performance. In comparing these two illustrations, it is interesting to note the rapidity with which the ore of finer mesh sizes yielded its manganese to give favorable leaching recoveries in regards to higher leaching temperatures. In Plate IV, the results show a fairly uniform spread of increasing recoveries with increasing fineness of ore and time of leaching. Plate V, however, shows the same effect on the coarser sizes of ore, but a distinct jump to higher recoveries within short leaching periods is noted with the finer ore sizes. From observation of these plates, it is apparent that the same 97.2 percent manganese recoveries attained

in leaching -100 mesh ore for 6 hours at 60°- 65°C., can be attained for the same ore in approximately 2 hours leaching time at 85°- 90°C. Increasing fineness of ore and higher temperatures, hand in hand lead to faster, and in turn, higher, recoveries of the manganese content of the ore.

Effect of Acid Concentration and pH Values

Plates VI, VII, and VIII, plotted from data tabulated in Table 5, show the results of the experiments carried on in search of an optimum acid requirements in line with high recoveries of the manganese content of the ore and attainment of the maximum pH values under this series of leaching procedure.

With regards to Plate VI, it is seen that the free acid values in the leached solution seem to approach a value in the neighborhood of 1.40 grams if sulphuric acid per liter and tend to hold fairly constant around that concentration. This is indicated by the sharp rise in the curve shown with respect to a very slight increase in pH of the pregnant solution. The presence of this last portion of original acid seems to indicate that the leach-

resistant particles in the ore hold up this amount of acid (approximately 1.40 grams per liter) and prevent it from doing any actual leaching of the manganese values in the ore.

Plate VII shows the relationship of pH control with manganese recovery in the leach solution. The results are clearly shown for the two-hour and four-hour leaching periods on -100 mesh ore at a temperature of 85°-90°C. In a pH range of 1.32-2.00, recoveries of 98.0-98.6 percent of the manganese content were shown to be reached. However, in the pH ranges above 2.00, the recoveries dropped very rapidly to 80.9 percent at a pH of 2.78 on the two-hour leaching period. The four-hour leaching tests showed a similar trend as shown on the curves, but they had a tendency to approach higher pH values corresponding to the same recoveries for both leaching periods.

From a survey of Plates VI and VII, it is indicated that a definite maximum pH value is to be taken into consideration in order to get 98.0 percent manganese recoveries along with low free-acid concentrations in the leach solutions. This pH value appears to be between 2.00 and 2.05. As

both diagrams have a tendency to show, it is very difficult, if at all possible within reasonable leaching periods, to bring the final pH value of the leach solution to a point sufficiently high enough to precipitate the iron in the leaching operation. This is probably due to the fact that manganese dioxide is less soluble than the manganese oxides, and the presence of leach-resistant material in the ore requires a certain amount of acid before any leaching of the manganese values is to be put into effect.

From this standpoint, it will then be necessary to precipitate the iron by addition of CaO, MnO, or some other inexpensive pH regulator which would raise the pH to 5.30 or over, that is, the point necessary to precipitate the iron as ferric hydroxide. (See p. 17)

Plate VIII illustrates the direct results obtained in the search for the most favorable and economical acid concentration in the leach solution that would yield beneficial manganese recoveries. Using the acid concentrations arrived at during discussion of the problem on page 30, the results are shown on the curves as representing two-hour and four-hour leaching periods.

periods on -100 mesh ore at 85°-90°C. Upon using the previously determined acid concentrations of 44 grams sulphuric acid per liter, maximum manganese recoveries were not attained, and in line with these low recoveries, higher pH values were reached. Specifically, manganese recoveries of 80.9 percent and pH values of 2.78 were reached using this acid concentration on the two-hour leaching tests. The four-hour tests showed manganese recovery of 84.5 percent and a pH value of 2.80, respectively. Indications of a nearly constant amount of remaining free acid are indicated and justified by these curves, whereupon at low recoveries, values of approximately 1.40 grams free sulphuric acid per liter are found to be approached by decreasing recoveries of manganese in the leach solution. Since this fact is indicated upon using 44 grams sulphuric acid per liter in the leaching solution, it is highly probable that acid concentrations below this figure will show that the manganese recoveries are going to fall off rapidly in regards to an economical standpoint and metallurgical basis, whereas they will be of no value to successful and beneficial leaching of the ore. However,

upon increasing the acid concentration to 47 grams per liter, a sharp rise in recoveries is noted and a slight increase in free acid content is held at a pH of 2.25. Between acid concentrations of 48 and 50 grams per liter, excellent recoveries (98.0 percent or better) are noted at pH values from 2.05-1.73 respectively. Further additions of acid do not seem to appreciably increase the recoveries in regards to an economical viewpoint, and are in these respects, mainly a non-beneficial use of sulphuric acid.

The question now arises as to where the optimum acid requirement will be with respect to beneficial recoveries. Since 96.2 percent recoveries and a pH of 2.25 were obtained upon using 47 grams sulphuric acid per liter, 98.0 percent recoveries and pH of 2.00 with the use of 48 grams sulphuric acid per liter, and 98.6 percent recoveries with a pH of 1.82 when using 49 grams sulphuric acid per liter, (all for the two-hour leaching period) it is only a question as to the comparative cost of the reagents used. Whether it is desirable to obtain the highest possible recovery and involve a slightly higher expense for acid and pH regulators

such as lime, or sacrifice some of the recovery and use a lower acid content, that is, between 46 and 47 grams per liter, and consequently a smaller amount of pH regulating agent, is a question I believe to be answered only through closely controlled pilot plant operations on this particular type of ore, and the further treatment of the ore in the purification and electrolysis process. By this manner, a detailed cost sheet could be worked out and the above problem solved to the satisfaction of economic plant operation. Indications, however, point to the choice of 49 grams sulphuric acid per liter for the attainment of the highest possible manganese recoveries with the least amount of acid consumption tied in with acid losses.

Acid Consumption and Losses

From the results obtained, it is indicated that 49.0 - 1.94 = 47.06 grams sulphuric acid per liter, or the minimum amount of acid consumed by the ore to give the highest recoveries, that is, 98.6 percent on two-hour leaching cycles. The four-hour cycles are here considered insignificant because no appreciable gain in manganese recoveries on

single stage leaching procedures is noted, while a slightly larger amount of acid is used, e.g., (49.0 - 1.63 = 47.37 grams sulphuric acid per liter) due to a longer contact of the acid with the ore. I do not believe that the above results merit four-hour leaching periods in favor of two-hour periods for single stage leaching cycles under the designated conditions. The main acid consumers in the ore are namely: $CaCO_3$, $MgCO_3$, other carbonates, silicates, and various other impurities shown in the given analysis of the ore. The possibility of manganese silicates and sulphides should not be overlooked at this point, as they would be acid consumers and mainly lower the recovery of the manganese in the leach solution. From the above figures for acid consumption, a value of approximately 2.00 grams sulphuric acid per liter could be entered as acid losses due to leach resistant and acid consuming particles in the ore.

Relationship of Manganese and Iron Recoveries

Plate IX illustrates the relationship between manganese content and iron content in the

leached solution. Data for the curve was obtained from results tabulated in Tables 2, 3, and 4. Although the points on the plotted diagram seem to be scattered, indications of the form used in plotting the points tend towards a straight line relationship between the two variables. In other words, a direct proportion exists between manganese recovery and iron recovery to give a series of definite values concerning both constituents. With increasing manganese recovery, higher concentrations of iron will be found in the solution, and this fact stands to reason because of the close relationship of iron and manganese in their leaching properties. With higher manganese recoveries, more impurities will be involved in the leach solution, and as explained before, (see p. 17) iron plays a very important part in the purification step by assisting in the removal of arsenic, a highly undesirable impurity in the electrolyte. The electrolyte must be very pure, but almost complete removal of the iron is afforded by pH control, and hence very clean removal of the arsenic also. The purification process

is an entire new research problem in itself, and opens the field to many more investigations along these lines. However, as stated earlier in this report, iron recovery was taken into consideration mainly to obtain some ideas as to its behavior in the leach solution and effects of its presence in the leaching procedure. Iron had no detrimental effects during the actual leaching of the ore, except the small part it played as an acid-consumer. The concentrations of iron recovered in the leached solution (0.96 grams per liter with 98.6 percent manganese recoveries) will account for very little of the total acid consumption.

The presence of iron in small quantities in the pregnant solution is therefore desirable as a purification agent and means of pH regulation.

Mesh thru	Ore gm/lit.	Temp. °C	Time hr.	Orig. Soln. lit..	Soln. Recd. lit..	Free Acid gm/lit.	Mn conc. gm/lit.	Fe.conc.. gm/lit.	Mn recovery percent
65	65	20-25	2	1.00	1.00	----	6.8	----	27.2
65	65	20-25	4	1.00	1.00	----	7.9	0.66	31.5
65	65	20-25	6	1.00	0.96	50.5	8.5	0.69	34.0
65	65	20-25	8	1.00	0.95	47.2	9.0	0.70	36.1
65	65	20-25	12	1.00	0.92	37.3	12.5	0.74	50.0

LEACHING DATA

(Note) All above tests were performed with continuous mechanical agitation, in acid solutions containing 70 gm. H_2SO_4 per liter, and 150 gm. $(NH_4)_2SO_4$ per liter.

Table 2.

Mesh thru	Ore gm/lit.	Temp. °C	Time hr.	Orig. Soln. lit.	Soln. Recd. lit.	Free Acid gm/lit.	Mn conc. gm/lit.	Fe conc. gm/lit.	Mn Recovery percent
6	65	60-65	1	1.00	1.00	50.5	8.8	0.53	35.2
6	65	60-65	2	1.00	1.00	31.1	16.0	0.67	64.0
6	65	60-65	4	1.00	0.99	30.4	18.2	0.72	72.8
6	65	60-65	6	1.00	0.98	28.9	19.2	0.77	76.8
28	65	60-65	1	1.00	1.00	48.5	9.2	0.60	36.8
28	65	60-65	2	1.00	0.99	30.6	16.9	0.68	67.6
28	65	60-65	4	1.00	0.98	24.3	19.8	0.74	79.3
28	65	60-65	6	1.00	0.97	22.4	21.3	0.78	85.2
65	65	60-65	1	1.00	1.00	40.1	10.0	0.65	40.0
65	65	60-65	2	1.00	1.00	28.9	17.6	0.81	70.4
65	65	60-65	4	1.00	0.98	22.0	21.8	0.88	86.2
65	65	60-65	6	1.00	0.97	20.7	22.6	0.92	90.3
100	65	60-65	1	1.00	1.00	35.8	14.8	0.66	59.2
100	65	60-65	2	1.00	1.00	21.3	20.0	0.83	80.0
100	65	60-65	4	1.00	0.97	17.8	22.8	0.88	91.3
100	65	60-65	6	1.00	0.97	14.2	24.3	0.98	97.2

LEACHING DATA

(Note) All above tests were performed with continuous mechanical agitation, in acid solutions containing 70 gm. H_2SO_4 per liter, and 150 gm. $(NH_4)_2SO_4$ per liter.

Table 3.

Mesh thru	Ore gm/lit.	Temp. °C	Time hr.	Orig. Soln. lit.	Soln. Recd. lit.	Free Acid gm/lit.	Mn conc. gm/lit.	Fe conc. gm/lit.	Mn Recovery percent
6	65	85-90	1	1.00	1.00	43.6	11.4	0.71	45.8
6	65	85-90	2	1.00	1.00	28.9	17.4	0.77	69.7
6	65	85-90	4	1.00	0.98	26.5	19.3	0.78	77.2
6	65	85-90	6	1.00	0.91	21.3	20.2	0.79	80.9
28	65	85-90	1	1.00	1.00	40.8	12.2	0.80	48.9
28	65	85-90	2	1.00	1.00	31.0	18.6	0.86	74.5
28	65	85-90	4	1.00	0.97	22.4	21.4	0.89	85.7
28	65	85-90	6	1.00	0.93	19.3	22.9	0.88	91.6
65	65	85-90	1	1.00	1.00	24.4	21.2	0.83	84.8
65	65	85-90	2	1.00	0.99	19.0	23.8	0.86	95.2
65	65	85-90	4	1.00	0.96	17.3	24.2	0.89	97.0
65	65	85-90	6	1.00	0.90	16.6	24.4	0.92	98.0
100	65	85-90	1	1.00	1.00	21.0	23.2	0.92	92.8
100	65	85-90	2	1.00	0.97	16.6	24.5	0.94	98.1
100	65	85-90	4	1.00	0.94	15.9	24.6	0.98	98.6
100	65	85-90	6	1.00	0.90	15.2	24.7	0.99	98.9

LEACHING DATA

(Note) All above tests were performed with continuous mechanical agitation, in acid solutions containing 70 gm. H_2SO_4 per liter, and 150 gm. $(NH_4)_2SO_4$ per liter.

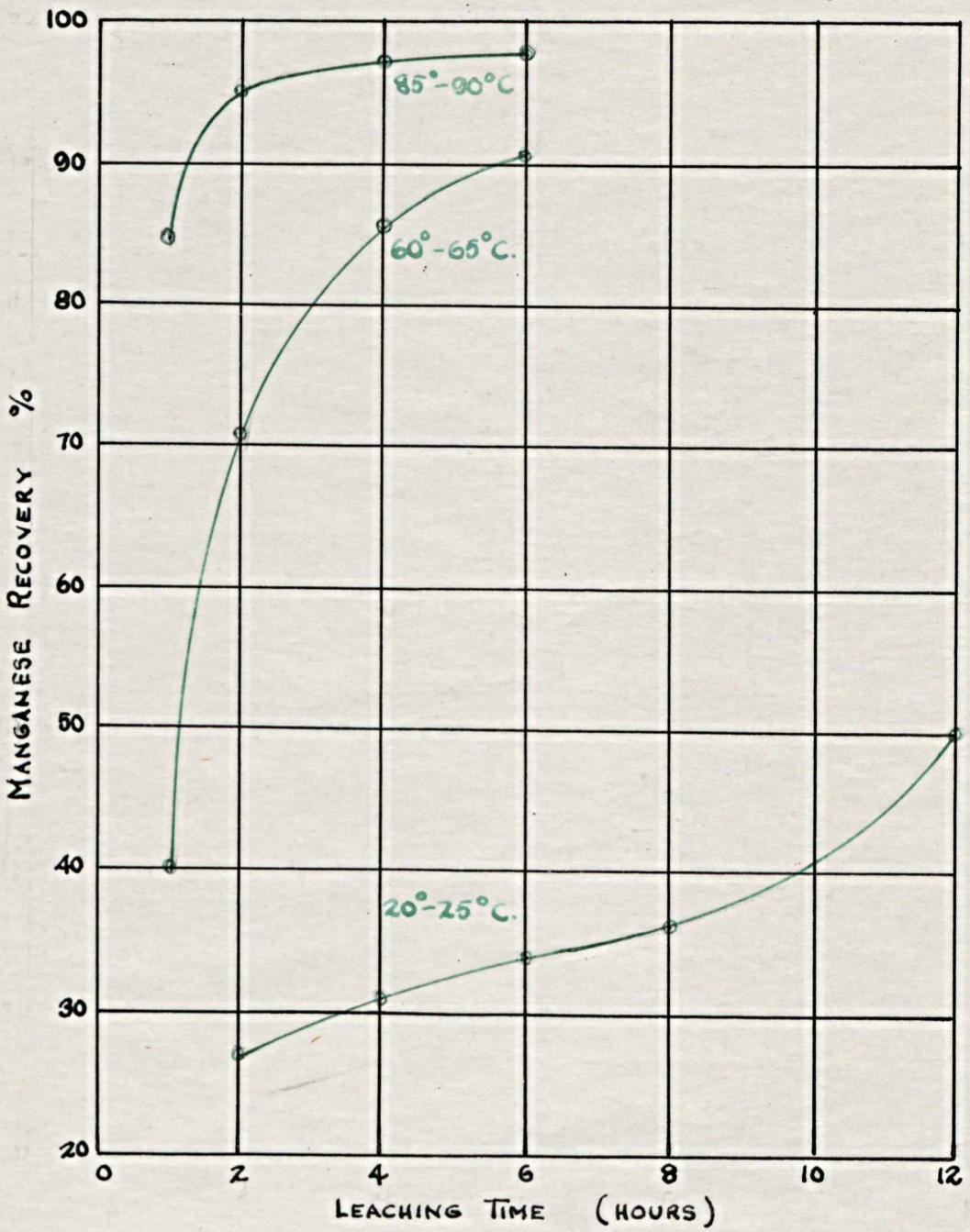
Table 4.

Mesh thru	Ore gm/lit.	Acid gm/lit.	Temp. °C	Time hours	Free Acid gm/lit.	pH	Mn gm/lit.	Fe gm/lit.	Mn Recovery percent
-100	65	56	85-90	2	3.20	1.32	24.6	0.97	98.6
-100	65	56	85-90	4	3.00	1.50	24.7	0.97	98.9
-100	65	50	85-90	2	2.00	1.73	24.6	0.96	98.6
-100	65	50	85-90	4	1.96	1.88	24.7	0.96	98.9
-100	65	49	85-90	2	1.94	1.82	24.6	0.94	98.6
-100	65	49	85-90	4	1.63	1.90	24.6	0.97	98.8
-100	65	48	85-90	2	1.48	2.00	24.4	0.92	98.0
-100	65	48	85-90	4	1.49	2.05	24.5	0.93	98.1
-100	65	47	85-90	2	1.44	2.25	24.0	0.90	96.2
-100	65	47	85-90	4	1.40	2.30	24.1	0.91	96.5
-100	65	44	85-90	2	1.40	2.78	20.2	0.72	80.9
-100	65	44	85-90	4	1.38	2.80	21.1	0.74	84.5

LEACHING DATA

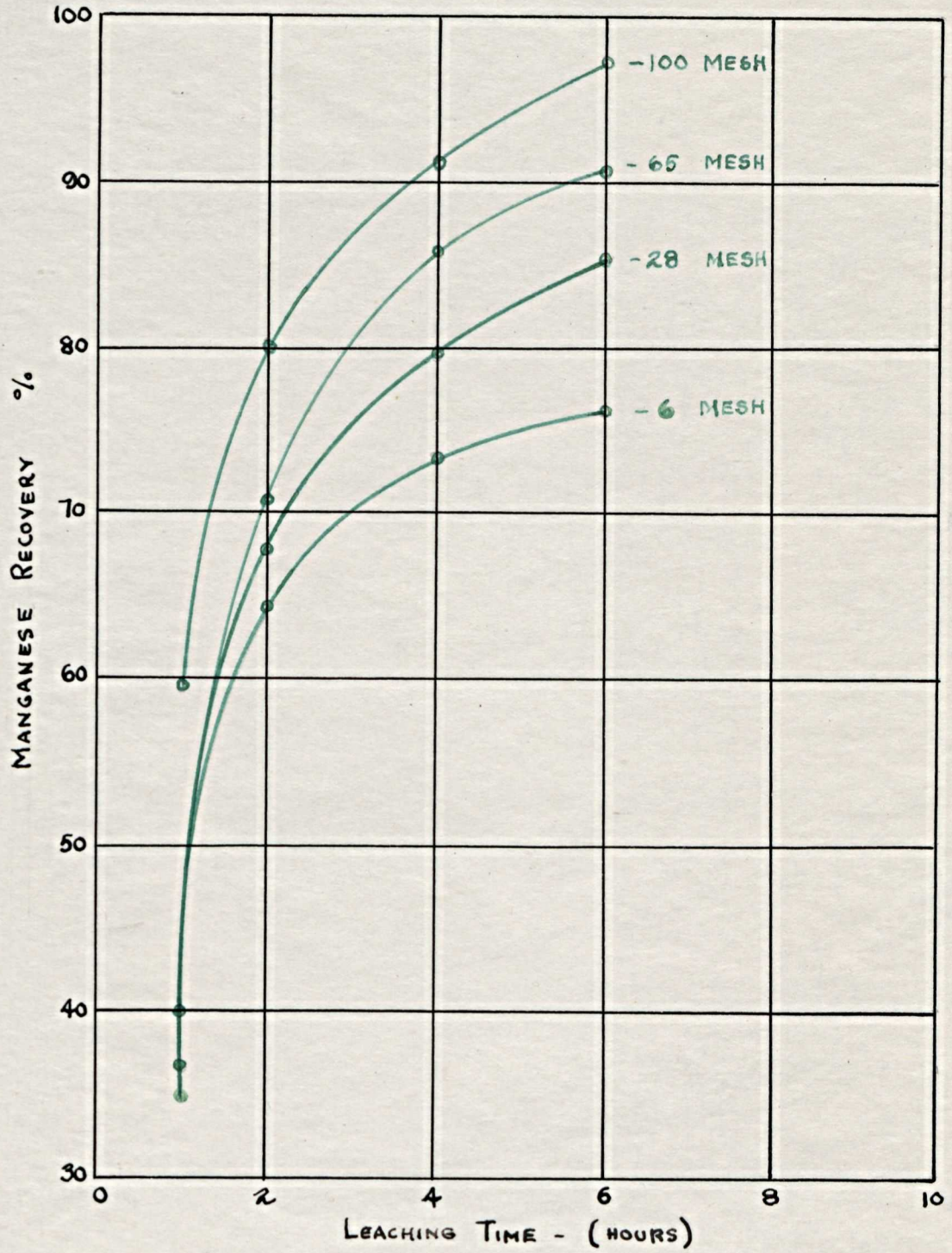
(Note) All above tests were performed with continuous mechanical agitation, in 1-liter solutions, containing no $(NH_4)_2SO_4$. The pH determinations were made with a Beckman pH-Meter.

Table 5.



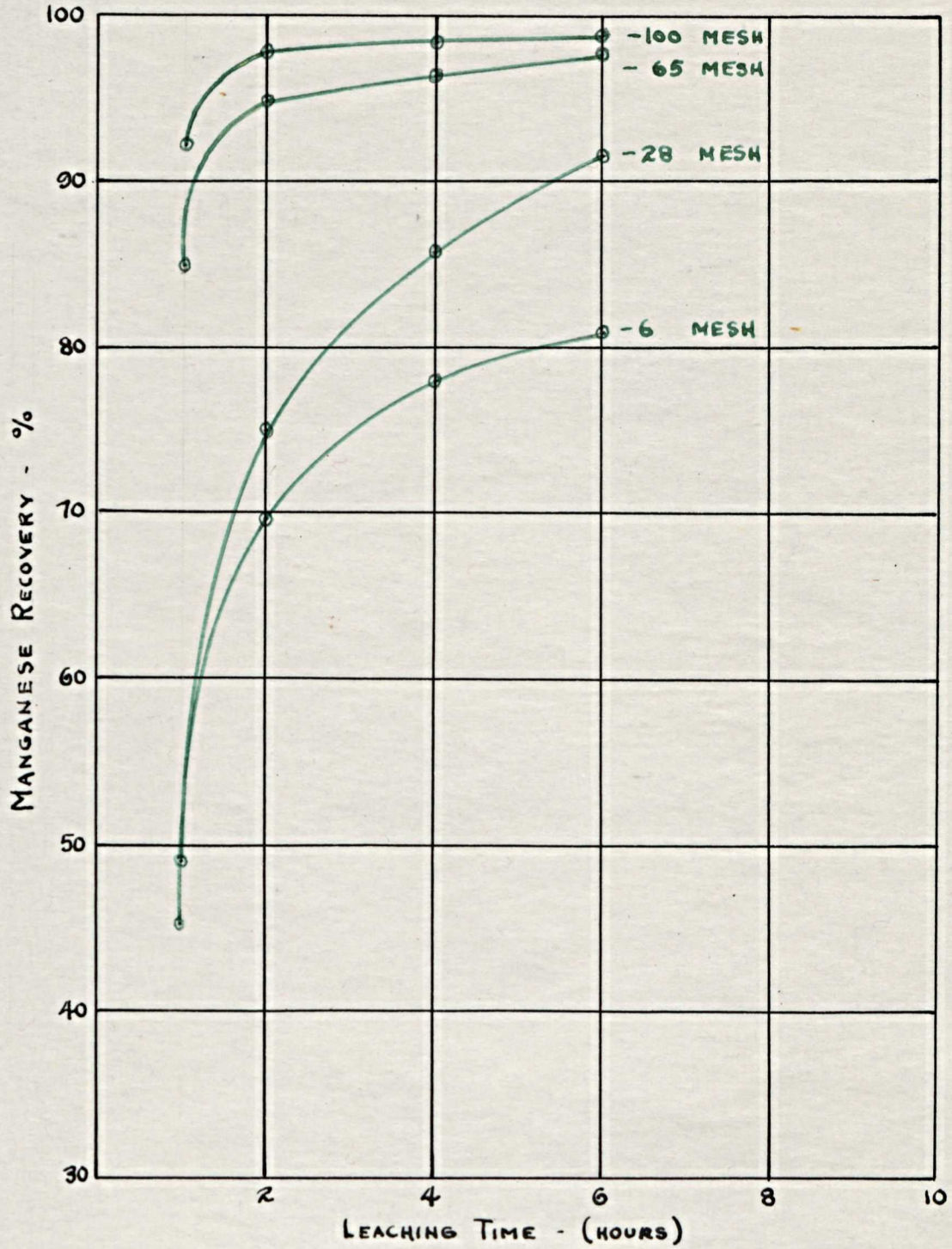
Effect of Leaching Time and Temperature upon Manganese Recovery (-65 mesh ore used)

Plate III



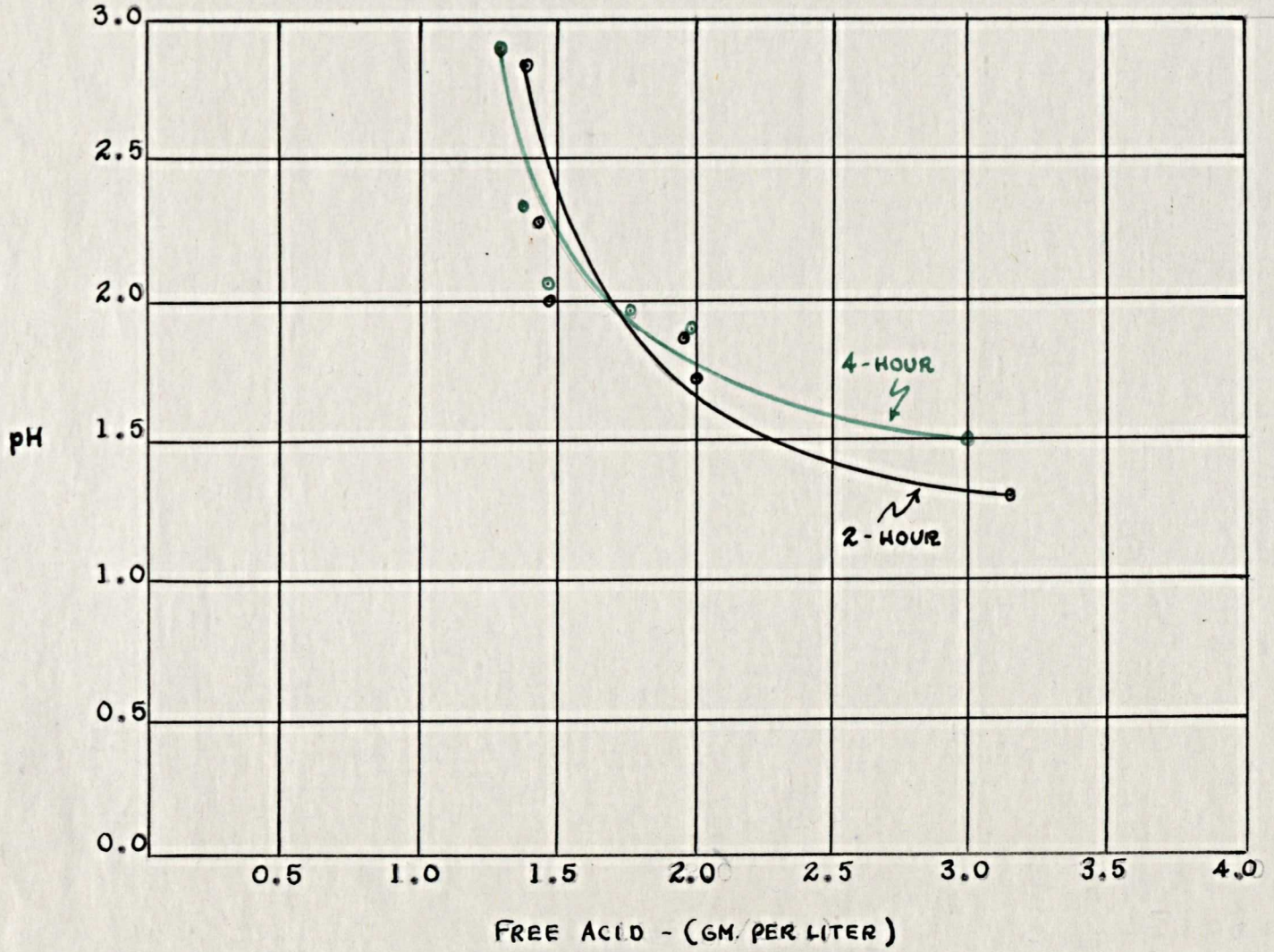
Effect of Mesh Size of Ore and Leaching Time upon Manganese Recovery (Temp. 60°-65°C)

Plate IV



Effect of Mesh Size of Ore and Leaching Time upon Manganese Recovery (Temp. 85°-90°C)

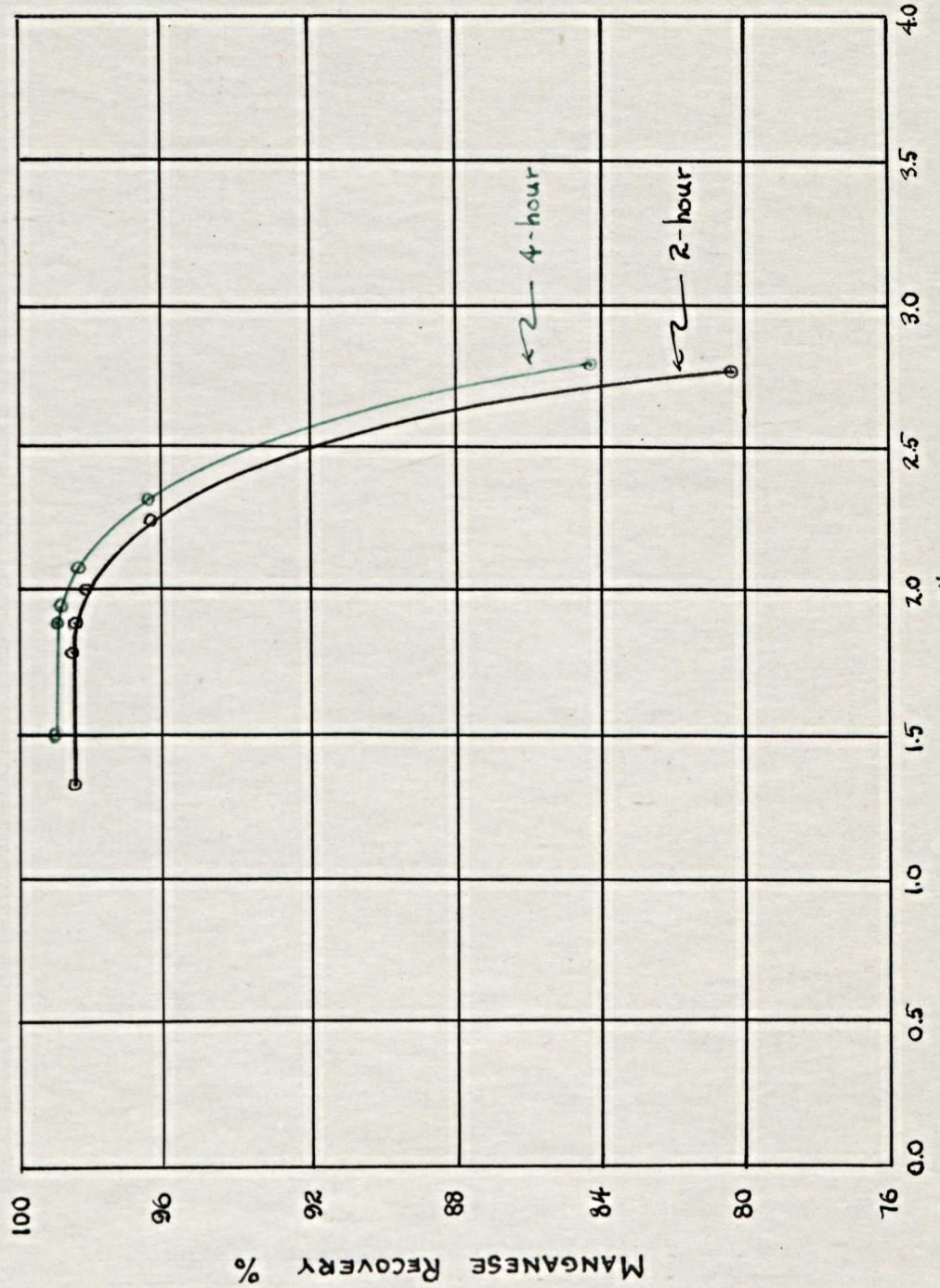
Plate V



Effect of Free Acid Content upon pH Values **

** See Table 5.

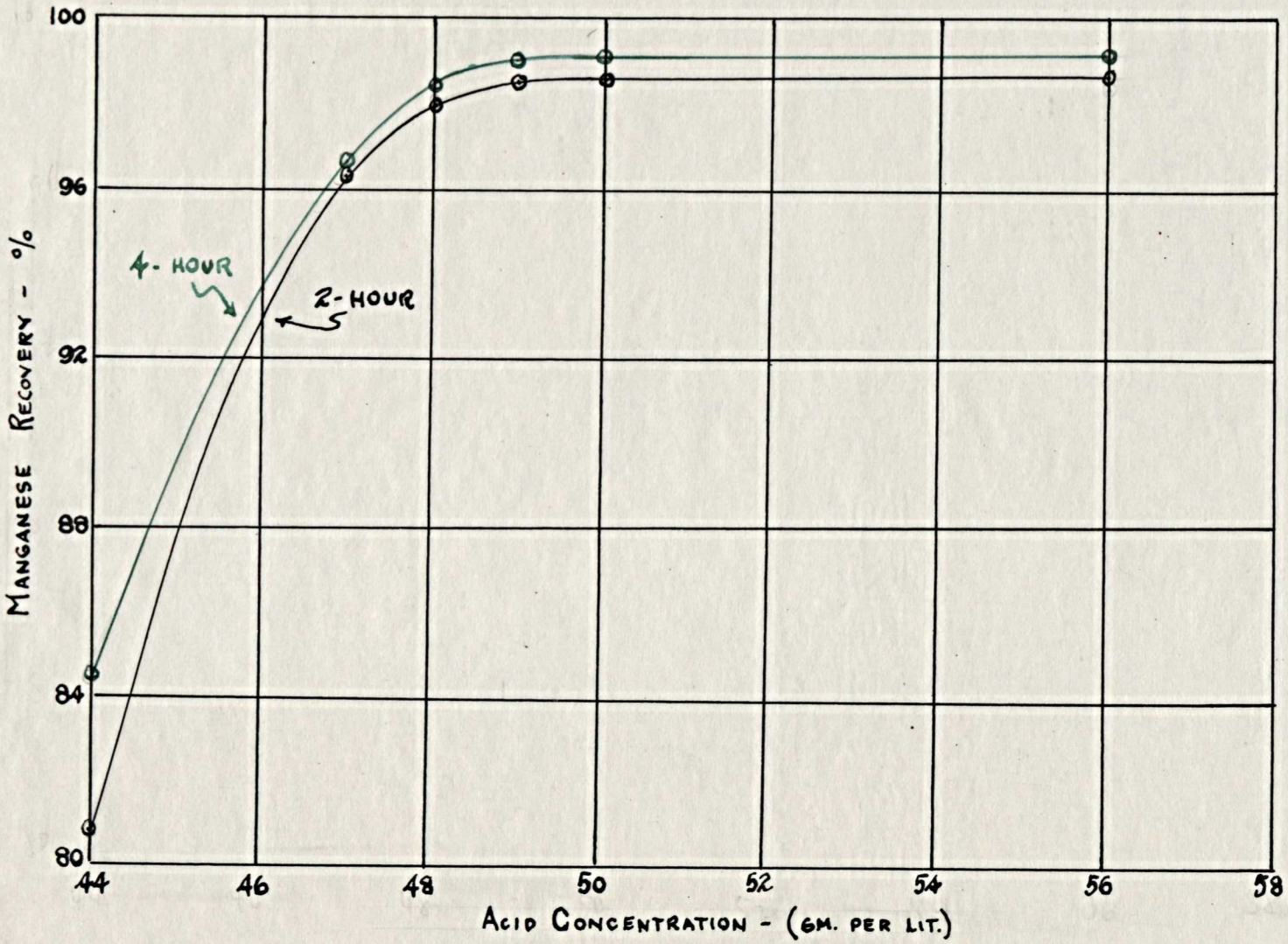
Plate VI



Effect of pH Values upon Manganese Recovery **

** See Table 5.

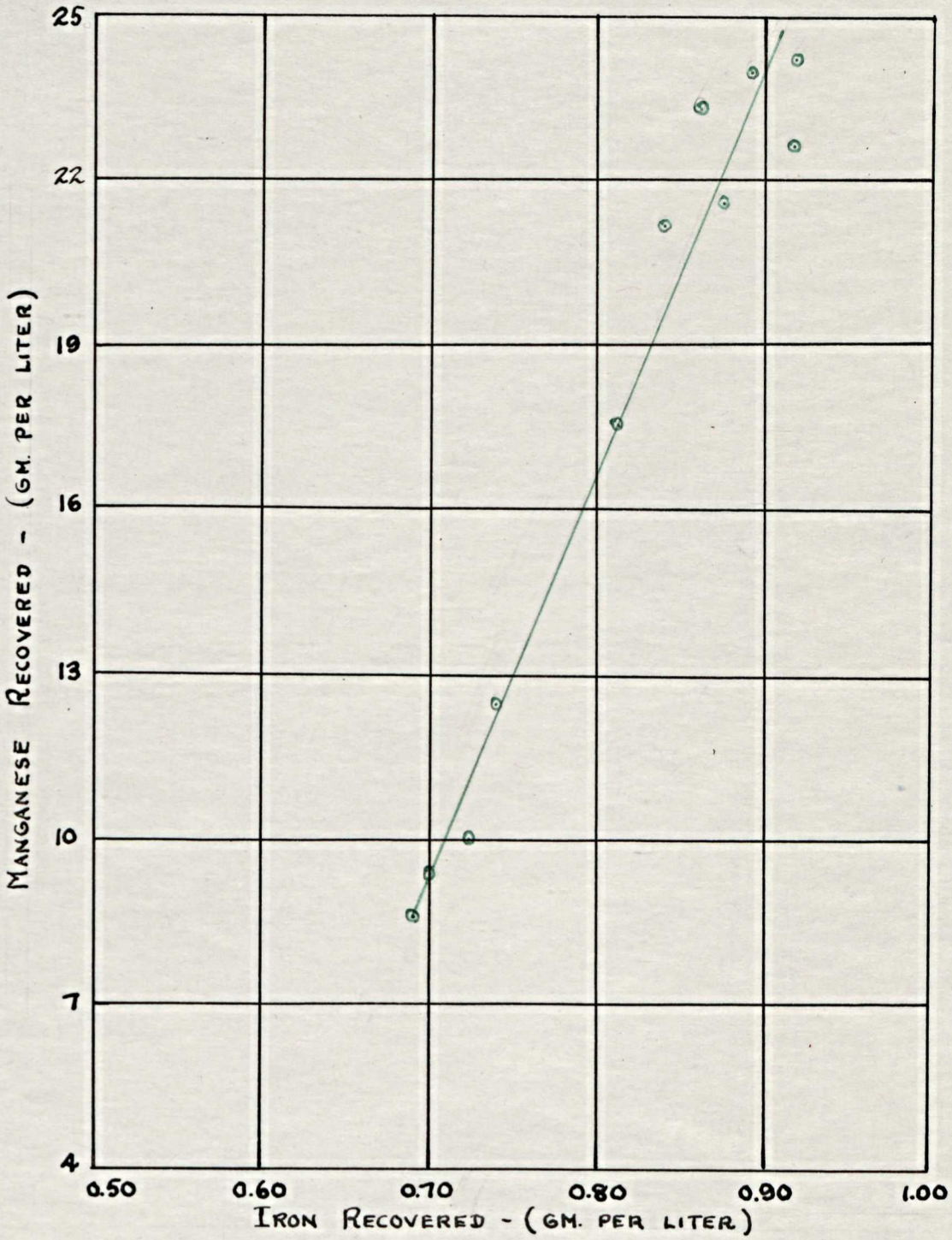
Plate VII



Effect of Acid Concentration in Leaching Solution upon Manganese Recovery **

** See Table 5.

Plate VIII



Effect of Manganese Recovery upon Iron Recovery

Plate VIII

CONCLUSIONS

(1) The Butte rhodochrosite can be satisfactorily leached to high manganese recoveries with the use of dilute sulphuric acid-ammonium sulphate leaching solutions and single-stage operations at elevated temperatures. Best results are obtained at temperatures of 75°C. or over for two to four hour leaching cycles.

(2) The optimum acid requirement for attainment of 98.0 percent or better manganese recoveries in the above solutions should be between 47-49 grams sulphuric acid per liter, and expected acid losses will be approximately 2.00 grams per liter.

(3) Final pH values of the leached solution cannot be brought up to the desired point to precipitate ferric hydroxide. Lime or some other inexpensive pH regulator will have to be introduced into the solution at the end of the leaching operation in order to raise the pH values.

(4) The rhodochrosite ore should be ground to at least 90 percent through 100 mesh so as to yield the highest recoveries within the above designated leaching conditions.

RECOMMENDATIONS

As a result of the previous work done on my part in single-stage leaching of the Butte rhodochrosite, I hereby offer the following suggestions:

(1) Another series of leaching tests should be accomplished along the same lines as those in this report, but two-stage leaching should be the object of the investigation, in which the first stage should be studied under conditions of an excess of ore and an endeavor towards higher pH values, while the second stage should be run to gain the recoveries of the more leach-resistant particles of the ore.

(2) Leaching of this type of ore involves problems similar to those encountered in leaching of zinc ores for the production of electrolytic zinc. Equipment such as that used in the zinc leaching operations could be easily put into use for leaching of rhodochrosite, provided that the pachuca leaching tanks were provided to operate under elevated temperature conditions.

(3) As mentioned before, a more detailed study of reagent consumption and costs could be accomplished for the economical aspect of the process.

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ACKNOWLEDGMENT

At this time, I wish to extend my thanks to the Montana School of Mines and staff for the opportunity to carry on this work. For their excellent suggestions and criticisms, I am sincerely grateful to Prof. J. P. Spielman, Head of the Department of Metallurgy, and Dr. A. E. Koenig, Head of the Department of Chemistry.